



TITLE:

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(Commemoration Issue Dedicated to
Professor Tohru Takenaka On the Occasion
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NOTE

Blue Sodium Molybdate Hydrates Prepared under Reductive Condition

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We newly found blue sodium molybdate hydrates which contain Mo of oxidation state <6 . The hydrates had the same structures as sodium heptamolybdate hydrates according to X-ray diffraction results. They were confirmed to have Mo^{5+} by electron spin resonance and ultraviolet-visible spectroscopy.

KEY WORDS: Mixed-valence / Sodium heptamolybdate / Sodium molybdate hydrate / X-ray diffraction / ESR spectra / UV-VIS absorption spectra

1. INTRODUCTION

Mixed-valence binary or ternary molybdenum oxides have been studied intensely because of their interesting properties such as low-dimensional metallic conductivity.¹⁻⁷ Among them, many studies on mixed-valence molybdate hydrates have been studied, especially focusing on their photo- or electro-chromic properties.⁸⁻¹⁰ However, only a few mixed-valence molybdate hydrates are known; such as alkylammonium heptamolybdate hydrates partially reduced by UV irradiation.⁸⁻¹⁰ There is no report on alkali molybdate hydrates with Mo of oxidation state <6 except for $\text{Rb}_2\text{Mo}_6\text{O}_{18} \cdot 10\text{H}_2\text{O}$ and $\text{Rb}_2\text{HMo}_6\text{O}_{18} \cdot 12\text{H}_2\text{O}$,^{11,12} although alkali molybdate hydrates are very familiar.¹³ We newly found mixed-valence sodium molybdate hydrates in the course of investigation on preparation condition of hydrated sodium molybdenum bronze which is one of mixed-valence ternary oxides. In this paper some details are reported.

2. EXPERIMENTAL

The blue hydrate was obtained by a following procedure. 20 g of MoO_3 and 60 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 200 ml distilled water. (MoO_3 is not soluble in water, but soluble in Na_2MoO_4 solution.) By reducing this solution with 7 g of $\text{Na}_2\text{S}_2\text{O}_4$ at 3-5 °C, the blue hydrate was precipitated. The precipitate was filtrated and washed with 3-5 °C water. The blue color faded a little by drying the precipitate.

The hydrates as-prepared and dried for two days in N_2 were investigated by powder X-ray diffraction (XRD), thermogravimetry (TG) differential thermal analysis (DTA), and

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chemical analysis. In order to confirm the existence of Mo of oxidation state < 6 in the hydrates, we investigated their electron spin resonance (ESR) and ultraviolet-visible (UV-VIS) absorption of their aqueous solutions.

XRD patterns were measured using a Rigaku RINT 1200M diffractometer with $\text{Cu-K}\alpha$ (40 mA, 40 kV) radiation. TG-DTA curves were obtained on a MAC Science TG-DTA 2000 with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Na and Mo contents of the hydrates were measured using a HITACHI 180-80 atomic absorption spectrophotometer with the 3302.3 Å line of Na and the 3132.6 Å line of Mo, respectively. The ESR spectra of the samples were recorded together with the ESR signals of Mn^{2+} at $-20\text{ }^{\circ}\text{C}$ on a JEOL NM-FE3 spectrometer with 100 kHz magnetic field modulation, operating at 9.2 GHz. UV-VIS absorption spectra were measured by using a HITACHI U-3210 spectrometer.

3. Results and Discussion

XRD patterns of the samples as-prepared and dried for two days in N_2 are shown in

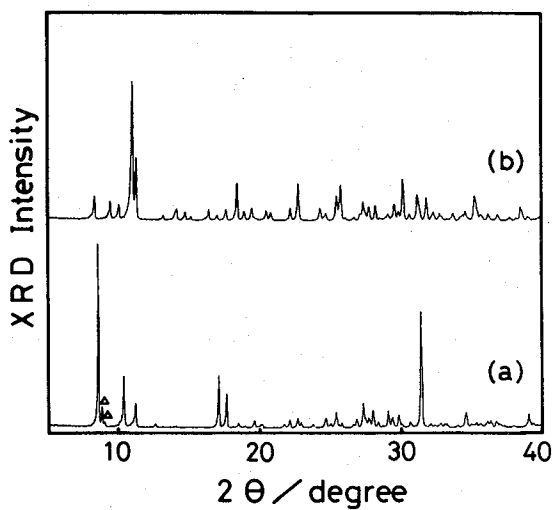


Fig. 1 XRD patterns of the samples as-prepared (a) and dried for two days in N_2 (b). Δ 's indicate undefined peaks.

Fig. 1. The pattern of the former sample is observed to comprise the peaks of an $\text{Na}_6\text{Mo}_7\text{O}_{24} \cdot 22\text{H}_2\text{O}$ -like structure¹⁴ and a few undefined peaks, while that of the latter sample is attributed to a single phase of $\text{Na}_6\text{Mo}_7\text{O}_{24} \cdot 14\text{H}_2\text{O}$ -like structure.¹⁴

According to the chemical analysis, the Na and Mo contents of the dried sample were 9.00 wt% and 44.7 wt%, respectively, and corresponded to those of $\text{Na}_6\text{Mo}_7\text{O}_{24} \cdot 14\text{H}_2\text{O}$ (Na 9.5 wt%, Mo 46.5 wt%). The as-prepared sample contained an indeterminable amount of adsorption water, which had no apparent thermogravimetric differences from some of crystal water of the sample. So we could not obtain significant Na and Mo contents of the sample.

Figure 2 shows TG-DTA curves of the dried sample in air and in N_2 . The total weight

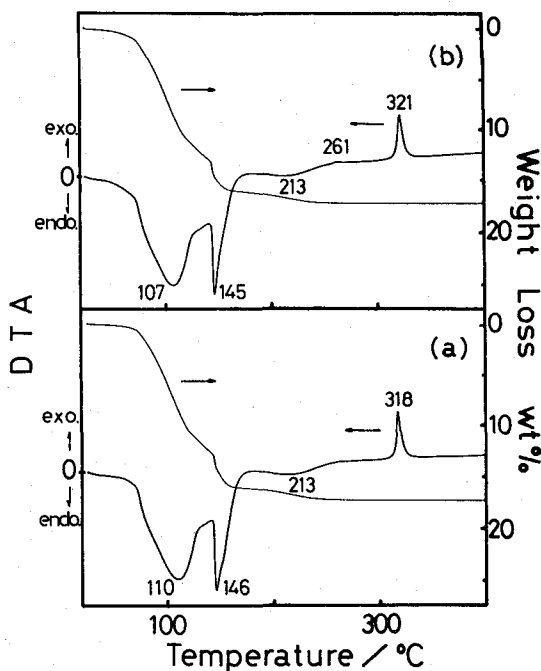


Fig. 2 TG-DTA curves of the dried hydrate, in air (a) and in N_2 (b).

losses of the sample by heating in air and in N_2 are 17.2 and 17.1 wt%, respectively. The weight losses (ca. 17 wt%) are attributed to dehydration and are compatible with the water content of $\text{Na}_6\text{Mo}_7\text{O}_{24} \cdot 14\text{H}_2\text{O}$ (17.4 wt%). The sample after the TG-DTA measurements in air and in N_2 were white and whitish-grey in color, respectively. The coloration of the sample heated in N_2 predicts the presence of Mo of oxidation state < 6 . An apparent difference between the TG-DTA results in air and in N_2 is a small exotherm at 261 °C, accompanied with no weight change, which is observed only in N_2 . We presume that this exotherm is related to structural defects arising from the existence of Mo of oxidation state < 6 , although any apparent structural differences between the samples heated in air and in N_2 could not be observed by XRD measurements. The as-prepared sample gave more complicated dehydration processes, but after dehydration there were no significant differences from the dried sample.

The confirmation of existence of Mo of oxidation state < 6 by ESR could be achieved for the as-prepared sample. Figure 3 shows its powder ESR spectrum. Weak and complicated

ESR signals of the sample are observed between the fourth and the sixth signals, from the lower magnetic field side, of Mn^{2+} . These signals are attributed to Mo^{5+} on the basis of the literature data.^{10,15-17} A more detailed interpretation about them is in progress.

Aqueous solutions of the hydrates gave deeper blue color than the hydrates themselves. Figure 4 shows a UV-VIS spectrum of an aqueous solution of the as-prepared sample (20 g.L^{-1} , 1 mm of optical path length). In the region above 400 nm two absorptions, which indicate the existence of Mo of oxidation state <6 , are observed at 620 and 750 nm. These absorptions are identical with those of a mixed-valence polymolybdate ion $[\text{Mo}_{13}\text{O}_{40}]^{4-}$, which is formed in the aqueous solution of photo-reduced ammonium or alkylammonium heptamolybdate hydrates by the reaction between $[\text{Mo}_7\text{O}_{23}(\text{OH})]^{6-}$, with Mo of the oxidation state of 5, and $[\text{Mo}_7\text{O}_{24}]^{6-}$.^{10,18} The spectrum of the dried sample was similar to this spectrum. From the above results, it is apparent that the blue hydrates have the same structures as sodium heptamolybdate hydrates $\text{Na}_6\text{Mo}_7\text{O}_{24} \cdot n\text{H}_2\text{O}$ and that they partially contain Mo of the oxidation state 5.

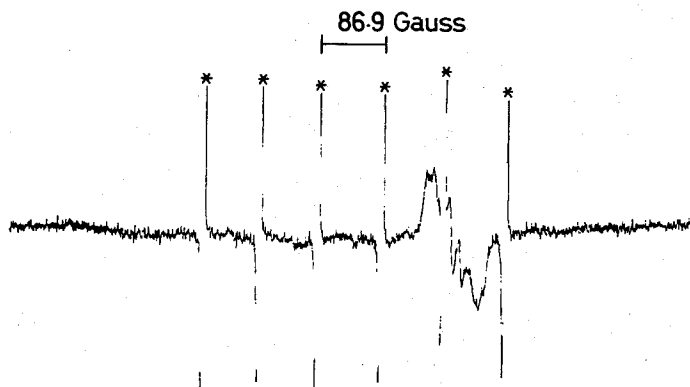


Fig. 3 An ESR spectrum of the as-prepared hydrate. *'s indicate the signals of Mn^{2+} .

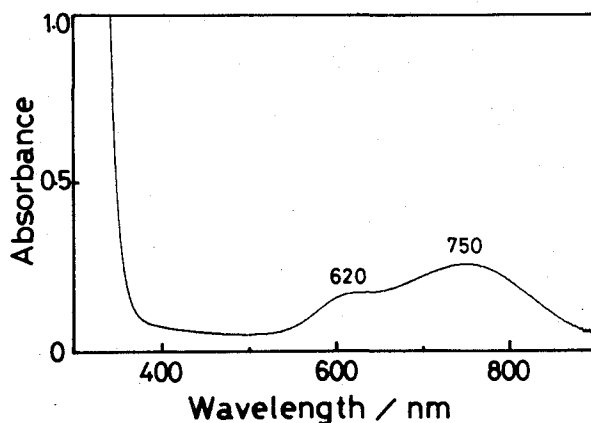


Fig. 4 UV-VIS absorption spectrum of the solution of the as-prepared hydrate.

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